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### (54) PRODUCTION OF BROMINATED POLYSTYRENE

#### (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a brominated polystyrene in a good efficiency and in a high yield, and a white powder without a purifying process, and useful as a flame retarder, etc., by dripping a solution obtained by dissolving a polystyrene and a Lewis acid catalyst with an organic solvent, into a bromine chloride solution and reacting them.

**SOLUTION:** This brominated polystyrene is obtained by dripping a solution obtained by dissolving a polystyrene and preferably 0.1-20mol% (based on the charged polystyrene) one or more kinds of Lewis acid catalysts selected from a halogenated antimony, a halogenated titanium, a halogenated boron and a halogenated boron complex into a bromine chloride solution and reacting them.

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[Claim(s)]

[Claim 1] The manufacture approach of the bromination polystyrene characterized by making the solution made to dissolve polystyrene and a Lewis acid catalyst in an organic solvent trickle and react to a bromine chloride solution in the approach of brominating polystyrene in an organic solvent and manufacturing bromination polystyrene.

[Claim 2] The manufacture approach of the bromination polystyrene according to claim 1 characterized by being at least one sort chosen from the group which a Lewis acid catalyst becomes from halogenation antimony, halogenation titanium, halogenation boron, and a halogenation boron complex.

[Claim 3] The manufacture approach of bromination polystyrene according to claim 1 or 2 that the amount of the Lewis acid catalyst used is characterized by being the 0.1-20-mol range of % to the polystyrene of preparation.

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[Detailed Description of the Invention]

[Field of the Invention] This invention relates to the approach of manufacturing bromination polystyrene useful as a flame retarder of synthetic resin.

[Description of the Prior Art] Conventionally, as an approach of manufacturing bromination polystyrene in an organic solvent, the method (JP,55-151007,A) of using bivalence and/or trivalent iron salt as a catalyst or the approach (JP,1-57684,B) using the Lewis acid catalyst which has activity equivalent to an antimony trichloride is learned, using a bromine chloride as a bromination agent.

[0003] The bromination reaction is performed by a bromine chloride solution being dropped at the solution which dissolved polystyrene and a catalyst, and after a reaction, both \*\* add and carry out crystallization of the obtained bromination reaction mixture to a poor solvent, and are collecting bromination polystyrene as fine particles.

[0004] [Problem(s) to be Solved by the Invention] However, the bromination polystyrene obtained by the conventional manufacture approach needed purification of removing a through coloring component for the reaction mixture after a bromination reaction to the activated carbon floor, in order for there to be a problem of wearing yellow coloring by the coloring component produced at a bromination reaction and to consider as a white product for this reason. Usually, since bromination of a bromine chloride is possible under a mild reaction condition, it can improve the coloring to a product compared with the bromine which are other bromination agents. However, if it did not refine in this approach as stated above, for not the whiteness degree that should be satisfied but this reason, it was not yet able to be said to be the industrial approach for obtaining quality bromination polystyrene by low cost.

[0005] This invention is made in view of the above-mentioned technical problem, and the purpose is in offering the approach of manufacturing white bromination polystyrene without purification processes, such as activated carbon, industrially.

[Means for Solving the Problem] This invention persons came to complete a header and this invention for the bromination polystyrene from which a coloring component is remarkably controlled and is obtained after crystallization as a result serving as white fine particles by dropping the solution which mixed polystyrene and a Lewis-acid catalyst into a bromine chloride solution, as a result of examining wholeheartedly the approach of manufacturing white bromination polystyrene without needing a purification process for a raw material for the polystyrene from which molecular weight is variously different.

[0007] That is, this invention is the manufacture approach of the bromination polystyrene characterized by making the solution made to dissolve poly Indanthrene and a Lewis acid catalyst in an organic solvent trickle and react to a bromine chloride solution in the approach of brominating polystyrene in an organic solvent and manufacturing bromination polystyrene.

[0008] Hereafter, this invention is explained to a detail.

[0009] Although especially the polystyrene used by the approach of this invention is not limited, what is usually in the range of 500-1,000,000 with the weight average molecular weight by standard polystyrene conversion is used.

[0010] The organic solvent used for a reaction by the approach of this invention can dissolve bromination polystyrene, and to a bromine chloride, it is inactive, or has very low reactivity, and, generally a halogenated hydrocarbon solvent is used. For example, a methylene chloride, chloroform, ethylene dichloride, 1 and 1, 1-Tori Chloe Than, 1 and 1, 2-Tori Chloe Than, a methylene bromide, bromoform, ethylene dichloride, etc. are mentioned. Especially as amount of the

organic solvent used, although it does not limit, that of \*\*\*\* for the amounts of two to 50 times is desirable at a weight ratio to the polystyrene possessed for a reaction according to reaction mixture viscosity, economical efficiency, etc.

[0011] Although the bromine chloride used as a bromination agent by the approach of this invention can usually prepare a bromine and chlorine by mixing below 5 degrees C, after it dissolves a bromine in the organic solvent used at a reaction beforehand, it may be mixed with chlorine. Even if the ratio of a bromine and chlorine uses a bromine superfluously in the range of a mole ratio 1.0 to 1.5 times rather than the amount of theory, it is satisfactory in order to lessen the chlorine content in a product, although its equimolar ratio is also essentially satisfactory. In addition, even if a bromine chloride also uses a commercial thing, it does not interfere.

[0012] Although a mole ratio is used for the amount of the bromine chloride used an equimolar ratio - 5 times to the number of nuclear bromination of the bromination polystyrene made into the purpose, it is equimolar ratio - 1.5 mole ratio preferably, and is decided by the class of catalyst to be used, and the reaction condition. In addition, the number of nuclear bromination of target bromination polystyrene is 2-3 pieces preferably, although 1-5 pieces are chosen.

[0013] A meltable thing is liked by especially the organic solvent, in order to make it dissolve in the polystyrene solution which is dropping liquid and to use especially as a Lewis acid catalyst used by the approach of this invention, although it does not limit. for example, an antimony trichloride and an antimony pentachloride -- halogenation boron complexes, such as halogenation boron, such as halogenation titanium, such as halogenation antimony, such as antimony, a titanium trichloride, and a titanium tetrachloride, boron trichloride, and 3 bromination boron, and a 3 fluoride boron diethylether complex, etc. are mentioned 3 bromination. Even if these are independent or it mixes and uses them, they do not interfere.

[0014] The amount of the catalyst used is changed with the number of nuclear bromination, reaction temperature, etc. which are made into the purpose. Usually, it is the 0.1-20-mol range of % to the polystyrene of preparation, and is 1-10-mol % preferably. less than [ 0.1 mol % ] -- a bromination reaction rate -- falling -- more than 20 mol % -- in the case where it adds, it may become the cause of insoluble matter generating by side reaction

[0015] Although the dropping temperature of polystyrene and catalyst mixed liquor changes with numbers of nuclear bromination made into a catalyst and the purpose, the range of it is usually -30-20 degrees C, and the range of it is -5-10 degrees C preferably.

[0016] That what is necessary is just to adjust according to the class of catalyst, an addition, and the generating condition of the heat of reaction at the time of dropping, although the drop time of polystyrene and catalyst mixed liquor is not limited especially, it is usually dropped in about 1 - 12 hours. After dropping, although after treatment may be performed immediately, aging may be performed at predetermined temperature for 1 to 12 hours.

[0017] It rinses by returning an excessive bromine chloride by adding reducing agents, such as a hydrazine and a sodium hydrogensulfite, after reaction termination, and a bromination polystyrene solution is obtained. Crystallization of this solution is added and carried out to a poor solvent or hot water, such as a methanol, and the bromination polystyrene of the specified substance is obtained as white powder by subsequently performing filtration and desiccation.

[0018] The bromination polystyrene obtained by the above approach is white powder with which coloring has been improved remarkably, and can be used as flame retarders, such as polyolefin resin and engineering plastics, as bromination polystyrene quality as it is.

[0019]

[Effect of the Invention] Since the bromination polystyrene obtained by the approach of this invention can be obtained without a purification process as white powder compared with the conventional approach, it can say this process as a technique very useful as the industrial manufacture approach of quality bromination polystyrene by low cost.

[0020]

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited only to these examples.

[0021] In addition, elemental analysis, weight-average-molecular-weight measurement, and hue analysis were performed by the following approaches.

(1) The elemental analysis of a bromine and chlorine performed the lean solution of gas by the well-known approach using ion chroma graph equipment (ion chromatography system by TOSOH CORP.), after carrying out oxygen flask combustion of the sample.

[0022] (2) Measurement of weight average molecular weight (standard polystyrene conversion) was performed by the well-known approach using gel permeation chromatography (high-speed-gel-permeation-chromatography system by TOSOH CORP.).

[0023] (3) Hue analysis of fine particles was performed by the well-known approach using the color difference meter

(Nippon Denshoku Industries colorimetry color difference meter; ND-1001DP mold).

[0024] It cooled at 0 degree C, preparing and agitating 49.2g (0.308 mols) of bromines, and 120g of methylene chlorides to the 300ml 4 opening round bottom flask equipped with example 1 thermometer, the impeller, and the cooling pipe. Subsequently, under churning of chlorine gas 21.9g (0.308 mols), it applied to this bromine solution for about 1 hour, and blew in into it, maintaining that temperature, and the bromine chloride solution was prepared. In addition, the preparation ratio of a bromine to chlorine was set as the equimolar ratio.

[0025] Then, weight-average-molecular-weight about 12,000 polystyrene 20.0g (0.192 mols per styrene unit), 2.2g (0.0096 mols) of antimony trichlorides, and 230g of methylene chlorides are prepared, and it was made to dissolve in a 300ml 4 opening round bottom flask under a room temperature, agitating. In addition, the preparation ratio of an antimony trichloride corresponds to five-mol% to the number of preparation mols per styrene unit of polystyrene. It was dropped at it at 0 degree C under churning after the dissolution, having covered [ this ] it over the bromine chloride solution prepared beforehand for about 3 hours, and aging was performed at that temperature after dropping for 1 hour. The residual bromine chloride was returned in the hydrazine water solution 20% after the reaction, acid cleaning and rinsing were performed, and 390g of reaction mixture of bromination polystyrene was obtained.

[0026] After making methanol 500g add and carrying out crystallization of the obtained reaction mixture, it filtered, and reduced pressure drying was carried out and 54.3g of white fine particles of bromination polystyrene was obtained. When elemental analysis was performed about this obtained bromination polystyrene, as a result of containing 66.1% of bromines, and 0.8% of chlorine and analyzing with gel osmosis chromatography, weight average molecular weight was about 13,000. Furthermore, as a result of a color difference meter's performing hue analysis of a product, for L value (lightness is shown), 91.8 and a value (green and + value show [ - value ] a red chromaticity) were [ -0.7 and b value (blue and + value show / - value / a yellow chromaticity) ] +2.1. A result is shown for a reaction condition in Table 1 in Table 2.

[0027]

[Table 1]

	ポリスチレン溶液 (前下流)										約15%濃度 <sup>1)</sup>	BrCl / (BrCl) <sup>2)</sup>	Br <sub>2</sub> / Cl <sub>2</sub>	熱媒 / (熱媒) <sup>3)</sup>	前下		熱成
	ポリスチレン <sup>1)</sup>			反応溶媒			溶媒								時間	温度	
	重量平均分子量	仕込み量	g	種類	仕込み量	g	Br <sub>2</sub>	Cl <sub>2</sub>	g	濃度							
実施例1	12,000	20	塩化メチレン	230	SbCl <sub>5</sub>	2.2	49.2	21.9	120	5.4	3.2	1.0	5.0	3.0	0	1.0	0
実施例2	200,000	20	塩化メチレン	230	SbCl <sub>5</sub>	4.4	49.2	21.9	120	5.4	3.2	1.0	10.0	5.0	1.3	0	1
実施例3	800,000	20	二酸化エチレン	230	SbCl <sub>5</sub>	2.2	49.2	21.9	120	10.0	3.2	1.0	5.0	3.0	0	3.0	0
実施例4	1,500	20	臭化メチレン	80	TiCl <sub>4</sub>	5.5	49.2	21.9	33	15.0	3.2	1.0	15.0	4.0	3.8	0	3
実施例5	12,000	20	塩化メチレン	100	BF <sub>3</sub> ·O(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	0.8	33.6	14.9	80	10.0	2.1	1.0	3.0	6.0	5.4	0	5
実施例6	12,000	20	塩化メチレン	230	SbCl <sub>5</sub>	2.2	58.1	21.9	120	5.4	3.2	1.2	5.0	3.0	-3.9	0	-3

1) ポリスチレンの重量平均分子量；標準ポリスチレン標準（ゲル浸透クロマトグラフ法による測定）。

2) BrCl 溶液の調製；Br<sub>2</sub> 溶液に、0℃の温度下、所定量のCl<sub>2</sub> ガスを1hrsかけて吹き込み調整を行った。

3) ポリスチレン濃度；並液及び前下流混合後の濃度を示す。

4) BrCl / ポリスチレン仕込み比；ポリスチレンのスチレンユニット当たりに対する値。

5) 熱媒 / ポリスチレン仕込み比；ポリスチレンのスチレンユニット当たりに対する値。

[0028]

[Table 2]

	収量 g	形状	元素分析値		重量平均分子量 <sup>1)</sup>	色相分析 <sup>2)</sup>		
			Br %	Cl %		L 値	a 値	b 値
実施例 1	54.3	白色粉体	66.1	0.8	13,000	91.8	-0.7	+2.1
実施例 2	55.1	白色粉体	66.5	0.9	210,000	91.5	-0.1	+2.5
実施例 3	53.5	白色粉体	66.2	1.0	810,000	91.0	+0.1	+2.8
実施例 4	54.5	白色粉体	66.0	0.8	1,800	90.9	+0.1	+2.3
実施例 5	48.9	白色粉体	58.8	0.9	13,000	91.1	+0.1	+2.3
実施例 6	55.5	白色粉体	66.9	0.3	13,000	91.5	-0.5	+1.9

1) 臭素化ポリスチレンの重量平均分子量：標準ポリスチレン換算（ゲル浸透クロマトグラフ法による測定）

2) 色相分析：L 値が明度、a 値に於いて一値が緑、+値が赤、b 値に於いて一値が青、+値が黄の強度を示す

<日本電色工業社製測色色差計（ND-1001DP型）を用いて測定>。

[0029] Except the reaction condition shown in example 2 - example 6 table 1, the bromination reaction was performed like the example 1, subsequently the same after treatment as an example 1 was carried out, and the white fine particles of bromination polystyrene were obtained. Furthermore, elemental analysis, weight-average-molecular-weight measurement, and hue analysis were performed by the same approach as an example 1. A result is shown for a reaction condition in Table 1 in Table 2.

[0030] It cooled at 0 degree C, preparing and agitating 49.2g (0.308 mols) of bromines, and 120g of methylene chlorides to the 300ml 4 opening round bottom flask equipped with example of comparison 1 thermometer, the impeller, and the cooling pipe. Subsequently, under churning of chlorine gas 21.9g (0.308 mols), it applied to this bromine solution for about 1 hour, and blew in into it, maintaining that temperature, and the bromine chloride solution was prepared.

[0031] Then, it was made to dissolve in a 300ml 4 opening round bottom flask, preparing and agitating weight-average-molecular-weight about 12,000 polystyrene 20.0g (0.192 mols per styrene unit), 2.2g (0.0096 mols) of antimony trichlorides, and 230g of methylene chlorides. In addition, the preparation ratio of an antimony trichloride corresponds to five-mol% to the number of preparation mols per styrene unit of polystyrene. It was dropped at it at 0 degree C under churning after the dissolution, having bromine chloride covered it over this solution for about 3 hours like the point, and aging was performed at that temperature after dropping for 1 hour. The residual bromine chloride was returned in the hydrazine water solution 20% after the reaction, acid cleaning and rinsing were performed, and 385g of reaction mixture of bromination polystyrene was obtained.

[0032] After making methanol 500g add and carrying out crystallization of the obtained reaction mixture, it filtered, and reduced pressure drying was carried out and 54.0g of yellow fine particles of bromination polystyrene was obtained. When elemental analysis was performed about this obtained bromination polystyrene, as a result of containing 65.8% of bromines, and 0.9% of chlorine and analyzing with gel osmosis chromatography, weight average molecular weight was about 13,000. Furthermore, as a result of performing hue analysis analysis of the product by the color difference meter, for L value, 81.3 and a value were [ +0.9 and b value ] +7.5. The obtained bromination polystyrene was remarkably inferior in the hue compared with the thing of an example so that clearly from the result of hue analysis. A result is shown for a reaction condition in Table 3 in Table 4.

[0033]

[Table 3]



	BrCl 溶液 (滴下液)				ポリスチレン溶液 (溶液)				PS濃度 /g/g "	BrCl /g/g "	Br /Cl モル比	結晶/非結晶 モル%	滴下		照成	
	Br	Cl	反応溶媒	溶媒	結晶	仕込み量 g	重量平均分子量 <sup>1)</sup>	仕込み量 g					時間	温度 ℃	時間	温度 ℃
	g	g	種類	仕込み量 g	種類	仕込み量 g	重量平均分子量 <sup>1)</sup>	仕込み量 g					hrs	hrs	hrs	hrs
比較例1	49.2	21.9	塩化メチレン	120	SbCl <sub>5</sub>	2.2	12,000	20	5.4	3.2	1.0	5.0	3.0	0	1.0	0
比較例2	49.2	21.9	塩化メチレン	120	FeCl <sub>3</sub>	1.6	12,000	20	5.4	3.2	1.0	5.0	3.0	0	1.0	0

- 1) BrCl 溶液の種類: Br<sub>2</sub> 溶液に、0℃の温度下、所定量の Cl<sub>2</sub> ガスを 1hr かけて吹き込み試験を行った。  
2) ポリスチレンの重量平均分子量: 標準ポリスチレン換算 (ゲル浸透クロマトグラフ法による測定)。  
3) ポリスチレン濃度: 溶液及び滴下液混合後の濃度を示す。  
4) BrCl/PS 仕込み比: ポリスチレンのスチレンユニット当たりに対する値。  
5) 結晶/PS 仕込み比: ポリスチレンのスチレンユニット当たりに対する値。

[0034]

[Table 4]

	収量 g	形状	元素分析値		重量平均分子量 <sup>1)</sup>	色相分析 <sup>2)</sup>		
			Br %	Cl %		L 値	a 値	b 値
比較例1	54.0	黄色粉体	65.8	0.9	13,000	81.3	+0.9	+7.5
比較例2	54.9	黄色粉体	66.1	1.0	13,000	82.3	+1.0	+9.5

- 1) 臭素化ポリスチレンの重量平均分子量: 標準ポリスチレン換算 (ゲル浸透クロマトグラフ法による測定)。  
2) 色相分析: L 値が明度、a 値に於いて一値が緑、+値が赤、b 値に於いて一値が青、+値が黄の濃度を示す  
<日本電色工業社製測色色差計 (ND-1001DP 型) を用いて測定>。

[0035] Except the reaction condition shown in example of comparison 2 table 3, the bromination reaction was performed like the example 1 of a comparison, subsequently the same after treatment as the example 1 of a comparison was carried out, and the yellow fine particles of bromination polystyrene were obtained. Furthermore, elemental analysis, weight-average-molecular-weight measurement, and hue analysis were performed by the same approach as the example 1 of a comparison. A result is shown for a reaction condition in Table 3 in Table 4. The bromination polystyrene obtained so that clearly from Table 4 was remarkably inferior in the hue compared with the thing of an example.

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[Translation done.]